A NOVEL BIODEGRADABLE LINEAR COPOLYMER,

A COMPOSITION COMPRISING IT, AND USES OF THE COPOLYMER

AND COMPOSITION

5   The   present   invention   relates   to   a   novel
biodegradable   linear   copolymer,   to   a   composition
comprising the copolymer, to different uses of this
copolymer and composition, and to different objects
comprising this copolymer.

10   Composite polymers able to degrade biochemically
are already known from the document WO 98/40434. These
polymers consist on the one hand of a first polymer
based on lactic acid monomers and on the other hand a
resin containing a thermoplastic polymer, destructured

15   starch and a plasticiser.

        Unfortunately   such   polymers   have   the   major
drawback   of   having   weak   mechanical   and   thermal
properties.   This   is   because   these   polymers   give

breakable products because of poor resistance to impact
and a glass transition Tg below 80°C.

A biodegradable mixture of synthetic polymers and
polymers of natural origin is also known from the
document US 5 446 078.

The synthetic polymers used in this mixture are
chosen from amongst non-biodegradable plastics, such as
polyolefins, rubbers and polyvinyl chloride. Thus,
even if the presence of natural polymers makes it
possible to biodegrade the non-biodegradable plastics,
the rate of degradation of such a polymer mixture still
remains too slow. This type of material also has too
many drawbacks vis-à-vis respect for the ecological
balance of the environment.

Finally, there is also known a thermoplastic
aliphatic polyester material,
polybutyleneglycolsuccinate, obtained at the end of a
chemical reaction between glycols and aliphatic
dicarboxylic acids. This material is known by the
trade name "Bionolle" and is sold by the company Showa
Highpolymer Co Ltd.

However, such a material has the drawback of
having a very high molar mass.

In addition, a reduction in the biodegradability
of a large number of materials already known for being
so has unfortunately already been observed, because of
the increase in their molecular mass, the increase in
the crystalline state, or the significant crosslinking
of the molecules in these materials.

This decrease in biodegradability can be observed, for example, on polyesters of the semi-aromatic type, and even more on aromatic polyesters.

Aliphatic polyurethanes and polyamides also have biodegradability properties which are not insignificant but which still remain less than those of polyesters.

Thus there exists a need to have a new aliphatic copolymer which is quickly and perfectly biodegradable, and which can be obtained easily and at lesser cost by means of conventional monomer polycondensation processes.

The object of the invention is therefore a novel copolymer comprising at least two identical or different monomers, the formula of the monomer being as follows (I):

$$Y - (CH_2)_c - C_e - (CH_2)_d - X \qquad (I)$$

with Z_a above C_e and $(COOH)_b$ below C_e
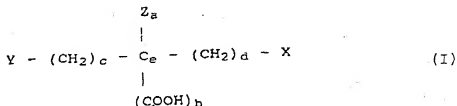
in which:

a) when X and Y are identical, and represent an acid, alcohol, amine or isocyanate group,

then at least two monomers have X, Y groups able to react with each other,

at least one of the monomers have the following characteristics:

$a \geq 1$

$b \geq 1$

$c + d \geq 0$

$e \geq 1,$

and Z can be OH, COOH, an alkyl having 1 to 18 carbon atoms, or any other unreactive group present during the polymerisation process,

the other monomers being of the same type or of the following formula (II):

$$Y - (CH_2)_n - X \text{ with } n \geq 1 \qquad (II)$$

b) <u>when X and Y are different</u> and represent, independently of each other, an acid, alcohol, amine or isocyanate group,

then at least one monomer comprises X, Y groups able to react with each other,

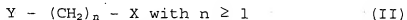at least one of the monomers have the following characteristics:

$$a \geq 1$$
$$b \geq 1$$
$$c + d \geq 0$$
$$e \geq 1,$$

and Z can be OH, COOH, an alkyl having 1 to 18 carbon atoms, or any other unreactive group present during the polymerisation process, the other monomers being of the same type or of the following formula (II):

$$Y - (CH_2)_n - X \text{ with } n \geq 1 \qquad (II)$$

c) at least one monomer of each type when X and Y are identical or different, as defined above, are combined so that the stoichiometry of the ratio X/Y,

calculated so as to obtain a given molar mass and given extremities, allows an elongation of the carbon-containing chain.

This novel copolymer has the advantage of being 100% biodegradable and having several pendent tertiary OH and COOH groups over the entire length of the carbon-containing chain. The presence of the pendent tertiary acid groups makes it possible to modify the physical properties of the copolymer because of the possibility of forming ion and/or hydrogen bonds. These new bonds confer on it properties of more or less crosslinked lattices.

In addition, the acid groups, put in the presence of monovalent cations or even better bivalent cations, allow the creation of a reinforcing ion structure of the type:

$$\begin{array}{c} | \\ C = O \\ | \\ O \\ \qquad B++ \\ O \\ | \\ C = O \\ | \end{array}$$
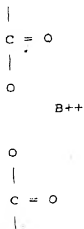
Finally, the presence of oxides, such as MgO, during the polymerisation process makes it possible to obtain, with the pendent groups of the copolymer,

structures which are substantially of the same nature as those described above.

The bonds formed between the pendent groups of the copolymer according to the invention and the ions and/or oxides make it possible to have a reinforced structure of the thermoplastic type. This type of structure has the great advantage of being completely destroyed during a rise in temperature because of physico-chemical transformations.

The ion and/or hydrogen bonds are moreover known for being able to be more easily accessible to bacteria, which can act more effectively in the slow process of biodegradation, whilst the covalent bonds present in the crosslinked polymers of the prior art for their part have a much slower biodegradation kinetics, which extends the duration of degradation accordingly. The variation in the physico-chemical properties of the copolymer of the invention, because of the creation/elimination of ion and/or hydrogen bonds, makes it possible to use it in applications of completely different natures.

Such a copolymer according to the invention also has the advantage of having an accelerated biodegradation kinetics when it is mixed with a natural polymer of the starch type, associated or not with gluten.

Starch and gluten (consisting essentially of amino acids and starch) are known for their biodegradable character. They are also known for being used as co-constituents of synthesised polymers, and

thus affording a reduction in the cost price and an
increase in the synergy of the biodegradation of such a
composition.

Finally, it is also known to have to use
additives making it possible to make the starch and/or
gluten chemically compatible with a synthetic polymer.
These additives comprise acid or anhydride groups.
Thus the use of a polymer like the one in the invention
already comprising COOH, and possibly OH, groups makes
it possible to perform compatibility chemical reactions
without any supplementary addition of compatibility
additives.

Finally, a stoichiometric ratio of the starting
monomers different from 1/1 makes it possible to obtain
a final copolymer range having different molecular
masses, and consequently different viscosities. The
chemical variation in the chain extremities and the
variant in the number of pendent groups on the monomers
makes it possible to use the copolymer of the invention
differently, equally well for example as an adhesive or
as a printing ink.

A last advantage of this copolymer is that it has
a total cost price appreciably lower than the
biodegradable copolymers existing so far. It is
approximately 35% to 50% lower in cost.

The copolymer of the invention is obtained
according to an already known method using a catalyst
chosen from amongst compounds of the zirconate or
titanate type, such as those sold under the brand name
"Tysor" by Dupont de Nemours. It is possible to use,

for example, titanium acetylacetonate, triethanolamine titanate, n-butyl polytitanate, chelated zirconate diethylcitrate and mixtures thereof.

The use of such a catalyst makes it possible not only to optimise the colour, which may be yellowish, but in particular to hydrolyse the catalyst at the end of the esterification reaction so as to obtain mineral oxides such as TiO_2, ZnO_2, which are inert vis-à-vis a reverse de-esterification reaction which may occur should the catalyst remain active.

The polymerisation process can take place in a conventional reactor or more economically using a "thin-film reactor", in particular in a dual-screw extruder whose length/diameter ratio is calculated so as to make it possible to perform all the manufacturing steps at one go. In particular, such a reactor makes it possible to add the starch and/or gluten lastly before the inactivation of the catalyst, which makes it possible to condense the amino acids present in the gluten in particular as polyamides in order to prevent their subsequent degradation during the transformation step.

Thus the catalysts used can be either esterification catalysts or amidification catalysts.

The polymerisation process can comprise different steps, including the feeding of raw materials, the conveying of these materials, their mixing and the discharge of the condensation water. Other steps can be the addition of starch and/or gluten or the addition

of additives chosen from amongst fillers, colorants and mixtures thereof.

The polymerisation· reaction can continue subsequently with a step of eliminating the water resulting from the reaction in which the amino acids present in the gluten are transformed into polyamides.

The copolymer of the invention resulting from these different manufacturing steps can then be directed to an extrusion/cutting step, the cutting being able to be effected either hot and dry, or in water.

Finally, a last step of drying the finished product may be necessary, as known to persons skilled in the art.

The nature of the screws and the temperature values used in such a reactor and the location of the different components intended to discharge the volatile reaction by-products are already known from the prior art, and particularly in the industrial manufacture of polyesters, for example of the PET or PBT type.

The quantities of water to be eliminated are preferably between approximately 10% and 25%, which is in general easy to achieve with a dual-screw extruder which makes it possible to eliminate up to 40% of residual solvents in the manufacture of polymers known from the state of the art.

The degree of polymerisation is adjusted continuously. Preferably, one of the monomers carrying tertiary groups is citric acid. The other monomers can be chosen from amongst the compounds of the prior art,

preferably using any type of monomer containing at least two primary acids and at least one tertiary group chosen from amongst the alcohol, acid and amine groups and mixtures thereof.

5   The physico-chemical characteristics of the copolymer of the invention can direct the choice of the monomer or monomers used at the start, and their respective concentrations defined, for example, by the stoichiometry or the amount of hydrogen and/or ion

10   bonds. The choice of the monomer can also be a function of the manufacturing cost of the copolymer.

        In so far as the use of ions and oxides can improve the cold mechanical properties of the copolymer of the invention, the amount of monomers containing

15   pendent COOH groups influences the amount of ions or oxides which can be used. In a preferred manner, the amount of these compounds is adjusted according to the amount of pendent COOH group, whilst taking account the amount of hydrogen bonds used.

20   The COOH/(ions and/or oxides) stoichiometric ratio of the copolymer of the invention is preferably close to 1.

        The amount of pendent acid groups has an influence on the amount of ions and oxides to be used

25   during the polymerisation. The variation in these amounts influences the properties of rigidity, flexion or biodegradability which are chosen as a function of the nature of the uses of the copolymer of the invention.

Another object of the invention is a composition which comprises the copolymer described above, combined with at least one ion chosen from amongst Na$^+$, Li$^+$, Ca^{++}, Mg^{++}, Zn^{++} and/or at least one oxide chosen from amongst magnesium oxide, zinc oxide and silicon dioxide.

The addition of compounds such as divalent ions, permitting the creation of ion bonds within the structure of the copolymer, makes it possible to strengthen its structure, as already explained above. The phenomenon of biodegradation always goes through a hydrolysis phase. However, the ion bonds, particularly sensitive to this type of degradation, thus facilitate the biodegradation of the copolymer of the invention because of the release of macromolecules principally of the polyester type, which behave in a conventional manner vis-à-vis biodegradation phenomena.

The composition according to the invention as defined above can also comprise starch (linear or branched) and/or gluten (starches + amino acids) or any other type of compound able to react, such as wood dust, wood fibres, cellulose fibres, polyvinylalcohol, ethylenevinylalcohol, polyamides, polyurethanes, functional or compatible polyacrylics, polycarbonates, polymethacrylates, polyacrylates and mixtures thereof.

This starch and/or gluten can also be added directly to the composition, which would comprise solely the copolymer according to the invention, without any divalent ion or oxides.

The copolymer may be present in a quantity ranging from 50% to 100% by weight, and preferably 60%

to 90% by weight, with respect to the total weight of
the composition.

The starch and/or gluten can be present in a
quantity ranging from 0% to 50% by weight, preferably

5 from 10% to 40% by weight, and even more preferably,
and for example for applications of the high-strength
copolymer on very thin objects of the smart card type,
from 20% to 35% by weight with respect to the total
weight of the composition. The adding of

10 polyvinylalcohol or ethylenevinylalcohol can be
effected at a low concentration so as to preserve
correct biodegradation properties of the copolymer of
the invention.

15 The copolymer according to the invention can have
a molecular mass of between approximately 500 and
100,000 according to the conversion rate, preferably
between 1000 and 40,000 and even more preferably
between 1000 and 10,000.

20 The composition according to the invention can
further comprise at least one additive chosen from
amongst colorants, mineral fillers such as titanium
oxide, calcium carbonate, pigments, antioxidants, anti-
ultraviolet agents and mixtures thereof. The additive

25 can be present in a quantity known from the field of
the prior art, which affords a good strength of the
manufactured material based on the copolymer of the
invention.

The glass transition (Tg) of the copolymer

30 according to the invention, obtained according to the

conventional methods, can preferably be subambiant. The Tg can be modified by adding divalent ions and/or oxides, by varying the stoichiometry parameters, the level of each pendent group, or the proportion of ionic crosslinking or hydrogen bonds. These different variations are known from the prior art.

The addition of ionised elements thus causes the high ionicity of the composition. This high ionicity promotes hydrolysis of the composition over time, and consequently the rapid biodegradability of the copolymer present in the composition.

The addition of compounds known for their rapid biodegradation, such as starch and/or gluten or others of the same type, reinforces the biodegradable feature of the composition of the invention and therefore of the copolymer provided that the degree of substitution of such molecules is less than or equal to 2.2.

Two other objects of the invention are a use of the copolymer according to the invention as an adhesive, and a use as a printing ink.

Finally, another object of the invention is a use of the composition as an adhesive and a use as a printing ink. The copolymer can have a degree of polymerisation ranging from approximately 5 to 25 when it is used in adhesive compositions, and a degree of polymerisation ranging from approximately 3 to 20 when it is used in printing compositions according to the nature and composition of the other elements in the composition.

The invention also relates to a smart card with contact, without contact or comprising both at the same time, to a card similar to smart cards having a support body comprising the copolymer as defined above.

Another object of the invention is an electronic label on a toy comprising the copolymer as defined above.

Finally a last object of the invention is an impermeable support sheet containing the copolymer as defined above. The printing of such a support sheet is carried out by the methods which are conventional in the field of smart cards.

The smart cards can be obtained by means of conventional injection, extrusion or lamination processes. The toys can be obtained by conventional moulding or extrusion.

The composition examples which follow are given solely as an indication and are in no way limitative vis-à-vis the invention.

The numerical values are given in numbers of moles.

In each example, the concentration of catalyst is 0.1% of the total number of moles.

EXAMPLE 1: (prior art)
- Citric acid   0
- Succinic acid   1
- Butanediol   1

The succinic acid/citric acid and COOH/OH stoichiometric ratios are respectively 100/0 and 1.

The mixture of initial compounds is heated at approximately 200°C for approximately 3 hours. This mixture changes progressively from the colourless state to a pronounced cloudy state.

5   The mixture is then drawn under vacuum for approximately one hour so as to discharge the water formed during the reaction. The final product solidifies over time in the form of a solid homogeneous compound, whitish in colour, whose melting point

10   measured by differential enthalpic analysis is approximately 109-110°C with a shoulder at approximately 105°C.

The melting enthalpy is approximately 68 J/g and crystallisation takes place at approximately 74°C.

15   The substance is 3% soluble in hexafluoroisopropanol (HFIP), and remains in the form of blocks in dissolution in acetone in a 50/50 proportion.

20   Only the lower molecular masses seem to be soluble in THF.

The substance resulting from this example has a hydrogen bond rupture glass transition which is invisible or only slightly visible.

25   EXAMPLE 2: (invention)
- Succinic acid   0.9
- Citric acid   0.1
- Butanediol   1
The succinic acid/citric acid and COOH/OH

30   stoichiometric ratios are respectively 90/10 and 1.

The same operating method is used as in Example 1. The substance obtained is slightly more yellowish in colour than that of Example 1, but is in the form of a homogeneous solid whose melting point is approximately 102-103°C.

The substance is 3% soluble in HFIP, but dissolves in a higher proportion in acetone. A whitish solution is obtained.

The substance resulting from this example shows a hydrogen bond rupture transition between 80° and 100°C just before melting.

EXAMPLE 3: (invention)

- Citric acid   1
- Succinic acid   0
- Butanediol   1

The succinic acid/citric acid and COOH/OH stoichiometric ratios are respectively 0/100 and 1.

The same operating method is used as in the previous examples. The final product is much more yellowish because of the interactions existing between the citric acid and n-butyl titanate.

The polymer is much more viscous. Unlike the two substances resulting from the previous examples, the polymer solidifies immediately. It has no melting point in the ambient area at ???°C unlike the two previous ones.

Its solubility in HFIP is identical to that of the other two. The 50/50 mixture in acetone gives a partial solubilisation very quickly, with a gelled

appearance. This substance dissolves completely when the quantity of acetone is increased.

The substance resulting from this example does not exhibit any melting in the regions of substances of the previous examples, but a hydrogen bond rupture transition between 100° and 170°C with a maximum at 130°C.

In conclusion from these three examples, the solubility parameters of a butanediol polysuccinate (Example 1) are completely modified by the introduction of citric acid. The behaviour of the final product (Example 1) is characteristic of a product "crosslinked" by hydrogen bonds [tertiary OH ----- COOH], these bonds rupturing in dilute solvent phase.

This is confirmed by the absence of a melting point (Example 3) and by the reduction in the melting point in Example 2.

The substances resulting from these three examples have a subambiant Tg.

According to the proportion of citric acid introduced, there is a partial fusion of the succinate chains which becomes lower and lower, but a physical crosslinking which is stronger and stronger through hydrogen bonds, and a progressive decrease in the value of the melting enthalpy.

The disappearance of the melting point is situated around a composition comprising approximately:

- succinic acid   0.2 mol (14.75 g)
- citric acid   0.2 mol (24 g)
- butanediol   0.4 mol (22.5 g)

For the substances resulting from the above three examples, a significant ester peak is found on the infrared spectra. The presence of the COOH and OH groups (3500 to 3000 cm^{-1}) is very significant in the substance of Example 3, less significant in the substance of Example 2 and very low in the substance of Example 1.

This proves that the citric acid does not react by means of its tertiary OH and COOH functions, but solely by virtue of its primary COOH functions.

Example 4: (invention)
- Citric acid   0.28
- Succinic acid   0.72
- Butanediol   1

Example 5: (invention)
- Citric acid   0.5
- Succinic acid   0.5
- Butanediol   1

The composition of Examples 4 and 5 does not have any melting point.

EXAMPLE 6: (invention)
- copolymer   75%
- gluten   25%

In this mixture a perfect compatibility is found between the polymer and gluten because of the presence of the pendent COOH and OH groups.

This composition, whitish in colour, has a melting point at approximately 103°C.

EXAMPLE 7: (invention)
- copolymer   75%

- linear starch   25%

In this mixture a perfect compatibility is found between the polymer and gluten because of the presence of the pendent COOH and OH groups.

This composition, whitish in colour, has a melting point at approximately 103°C.

BRINGING OUT THE MAIN CHARACTERISTICS OF THE COPOLYMER OF THE INVENTION

Five manipulations were made, using citric acid and succinic acid in variable proportions, in a $COOH_{total}$/OH stoichiometric ratio of 1, and to which butanediol was added.

Table I below contains the molar proportions of each of the initial constituents of the above five examples:

Examples	Citric acid	Succinic acid	Butanediol	Stoichiometry
1	0	1	1	1/1
2	0.1	0.9	1	1/1
3	0.28	0.72	1	1/1
4	0.5	0.5	1	1/1
5	1	0	1	1/1

Table I

The aim of this study is to produce the infrared spectra of the citric acid, succinic acid and polymers resulting from each manipulation.

The copolymers resulting from each example are all obtained according to the following same operating method:

The different monomers and the catalyst are introduced into a glass tube. The whole is placed

under nitrogen and under stirring, the mixture is heated at 200°C for 3 hours and then vacuum is applied for 1 hour at 200°C.

It can be noted that the higher the concentration of citric acid, the faster the solidification of the final product.

- Figure 1 depicts the infrared spectrum of pure succinic acid on a pellet of KBr,

- Figure 2 depicts the infrared spectrum of pure citric acid,

- Figure 3 depicts the infrared spectrum of butanediol,

- Figure 4 depicts the infrared spectrum of the catalyst, titanium IV butoxide,

- Figure 5 depicts the infrared spectrum of Example 1,

- Figure 6 depicts the infrared spectrum of Example 2,

- Figure 7 depicts the infrared spectrum of Example 3,

- Figure 8 depicts the infrared spectrum of Example 4,

- Figure 9 depicts the infrared spectrum of Example 5,

- Figure 10 depicts the straight lines obtained after calculation of the intensity of the troughs in the zone 2800-3600 cm^{-1},

- Figure 11 depicts the curve obtained from the calculations made on the bands situated in the zone 1700-1800 cm^{-1},

- Figure 12 depicts the curve obtained by differential enthalpic analysis of the substance of Example 1,

- Figure 13 depicts the curve obtained by differential enthalpic analysis of the substance of Example 2,

- Figure 14 depicts the curve obtained by differential enthalpic analysis of the substances of Examples 3, 4 and 5.

Figure 1 shows the presence of the following bands:

- an acid band designated by the general reference 1a divided at 1700-1720 cm^{-1} corresponding to the C=O bond,

- several free linked OH bands 2a between 3000 and 3600 cm^{-1},

- characteristic bands 3 of alcohol and C=O groups situated at 1200, 1300, 1420 cm^{-1} and their corresponding harmonics at 2500, 2600 cm^{-1}, etc.

Figure 2 shows the presence of the following bands:

- an acid band 1b much wider than that of succinic acid at 1730-1735 cm^{-1} with two shoulders at around 1680 cm^{-1} and at around 2000 cm^{-1}. This demonstrates the presence of very strong hydrogen bonds,

- a free linked OH band 2b between 3000 and 3600 cm^{-1} which is much more intense because of the presence of the (tertiary) OH and COOH pendent groups,

- CH$_2$ bands 4 embedded in the OH band,

- other much more confused bands 5 (in the form of a solid body) related no doubt to the corresponding presence of hydrogen bonds.

5   Figures 5 to 9 show the changes in the following bands according to the concentration of each constituent:

- the linked OH band increases in intensity with the citric acid concentration,

10   - the ester/acid band is difficult to interpret although very sharp. The definition becomes much more clear when the bands in the concentrated zones, such as 2800-3600 cm^{-1} and 1700-1800 cm^{-1}, are examined.

a) In the zone 2800-3000 cm^{-1}, a very appreciable

15 increase in the bonded OH groups is noted compared with the CH$_2$ groups, and in particular with respect to the symmetrical CH$_2$ groups of butanediol, whose concentration remains constant in each example.

b)   In the zone 1700-1800 cm^{-1}, the

20 differentiation of the esters and acids is sharper:

- there exists a very sharp divided acid peak 6 at 1715-1720 cm^{1} corresponding to succinic acid, for the substances of Examples 1, 2 and 3, which is scarcely perceptible with the substance of Example 4 and which

25 disappears with Example 5,

- there exists an ester + acid peak 7 which increases between Examples 3, 2 and 1, whilst for Examples 3, 4 and 5 the intensity of this peak remains constant because of the maximum saturation. For equal

saturation, a broadening of the ester bands is however noted as a function of the citric acid concentration.

Different calculations have been made for the 2800-3000 cm^{-1} and 1700-1800 cm^{-1} bands in order to determine the intensity of the OH, COOH and CH_2 peaks. The bands being saturated, the calculation is made on the ratios of the half band lengths.

I – Study of the infrared spectra in the 2800-3600 cm^{-1} region

This study makes it possible to distinguish superimposed broad bands corresponding to the OH, CH_3- CH_2- and COOH groups (free and linked by the hydrogen bonds) as well as symmetrical and asymmetric broad CH_2 bands.

The only symmetrical CH_2 bands which the system has are those of butanediol marked by asterisks (*) in the following formula:
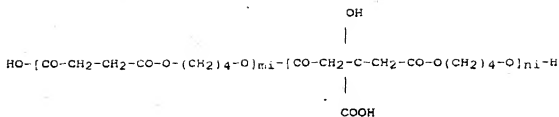
$$HO-CH_2-CH_2*-CH_2*-CH_2-OH$$
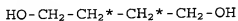
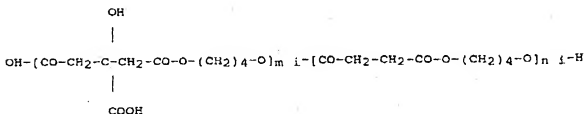Butanediol being in each example always in equal quantities, it thus serves as an internal reference.

When the structure of the final compound formed by polycondensation is examined, several cases can be presented according to the reaction kinetics and the ratio between each constituent.

The copolymer can be represented by the following general formula (I) in the case of an excess of succinic acid with a stoichiometry strictly equal to 1:

$$HO-[CO-CH_2-CH_2-CO-O-(CH_2)_4-O]_{m,i}-[CO-CH_2-\overset{\overset{\textstyle OH}{|}}{C}-CH_2-CO-O(CH_2)_4-O]_{n,i}-H$$

$$\underset{COOH}{|}$$

<div align="right">Formula (I)</div>

Or by formula (II) in the case of an excess of citric acid with a stoichiometry strictly equal to 1:

$$OH-[CO-CH_2-\overset{\overset{\textstyle OH}{|}}{C}-CH_2-CO-O-(CH_2)_4-O]_{m,i}-[CO-CH_2-CH_2-CO-O-(CH_2)_4-O]_{n,i}-H$$

$$\underset{COOH}{|}$$

<div align="right">Formula (II)</div>

The presence of an acid extremity and an alcohol extremity can be noted, the acid extremity being able to vary on one monomer as a function of the ratio between the two acids. The number of citric and succinic extremities is fixed by the proportionality rule, the number of alcohol extremities being equal to the total number of acid extremities for an ideal stoichiometry of 1. This rule may be modified if the reactivity of the two acid groups is different. This is because the monomer which reacts the most quickly has less chance of finding its extremities at the chain end even if it is present in excess. Likewise, according to the elongation of the chain of the most reactive acid, the stoichiometry may change during the

polymerisation reaction and it is possible to obtain two extremities of identical natures, mainly acid.

Thus, starting from this principle and if the polycondensation mechanism is considered, the total number of acid molecules (and consequently the total number of alcohol molecules) introduced initially can be termed "N_0", the number of groups of each type "$2N_0$" and the number of residual groups at the end of the reaction "N".

"N" can be equal or odd depending on whether the extremities consist of an acid group or an alcohol group, two acid groups or two alcohol groups.

Tables II and III below are then obtained:

Initial	Citric acid	Succinic acid	Butanediol	Total CH_2	Total acid	Total alcohol	Total ester
Acid extremities	$2N_0 x$	$2N_0(1-x)$	-	-	$2N_0$	-	-
Alcohol extremities	-	-	$2N_0$	-	-	$2N_0$	-
Pendent acid	$N_0 x$	-	-	-	$N_0 x$	-	-
Pendent alcohol	$N_0 x$	-	-	-	-	$N_0 x$	-
Esters	-	-	-	-	-	-	-
CH_2	-	-	-	$2 N_0$	-	-	-
Total				$2 N_0$	$2N_0+N_0 x$	$2N_0+N_0 x$	O

Table II

Final	Citric acid	Succinic acid	Butanediol	Total CH_2	Total acid	Total alcohol	Total ester
Acid extremities	N x	N(1-x)	-	-	N	-	-
Alcohol extremities	-	-	N	-	-	N	-
Pendent acid	N_0x	-	-	-	N_0x	-	-
Pendent alcohol	N_0x	-	-	-	-	N_0x	-
Ester	-	-	-	-	-	-	$2N_0$-N
CH_2	-	-	$2 N_0$	$2 N_0$	-	-	-
Total				$2N_0$	$N+N_0$ x	$N+N_0X$	$2N_0$-N

5 Table III

In infrared spectroscopy, each acid group has its "mark" which makes it possible to identify it from the others. This identification is established by means of 10 the constant "ε". The intensity of the band of this group is determined by the following general formula:

$$1 = \varepsilon \ e \ [c]$$

15 where "ε" is the constant of a precise acid group, "e" is the thickness of the film analysed and [c] the acid group concentration.

For the acid and alcohol groups present in the 20 region 2800-3600 cm^{-1}, the ratio of the heights or

widths of peaks of troughs gives the following formulae:

$$I_{COOH} = \varepsilon_1 \, e \, [COOH]_{e.c.} + \varepsilon_3 \, e \, [COOH]_{pendent} + \varepsilon_2 \, e \, [COOH]_{e.s.}$$

$$I_{OH} = \varepsilon_2' \, e \, [OH]_{e.a.} + \varepsilon_4 \, e \, [OH]_{pendent}$$

$$I_{CH2} = \varepsilon_0 \, e \, [CH_2]$$

Where "e.c." means citric extremity, "e.s." succinic extremity and "e.a." alcohol extremity.

The calculation of the ratios gives:

$$I_{COOH}/I_{CH2} = (\varepsilon_1 Nx + \varepsilon_2 N(1-x) + \varepsilon_3 N_0 x) \, / \, \varepsilon_0 (2N_0)$$

$$I_{OH} \, / \, I_{CH2} = (\varepsilon'_1 \, N + \varepsilon_4 \, N_0 x) \, / \, \varepsilon_0 \, (2N_0)$$

That is to say

$$I_{COOH}/I_{CH2} = [(\varepsilon_1 - \varepsilon_2) \, / \, DP_n \, 2\varepsilon_0) + \varepsilon_0/2\varepsilon_0] \, x + (\varepsilon_2 \, / \, DP_n 2\varepsilon_0)$$
$$I_{OH}/I_{CH2} = \varepsilon_2' \, N \, / \, 2\varepsilon_0 N_0 + \varepsilon_4 x \, / \, 2\varepsilon_0 = \varepsilon'_2 \, / \, 2\varepsilon_0$$

The degree of polymerisation "DP_n" is given by the following formula:

$$DP_n = 1/f \, (1/1-\alpha) \text{ where } \alpha \text{ is the conversion degree, and}$$
f the functionality of the reagents.

α is defined by: $\alpha = [ester]/\text{number of groups}$

that is to say $\alpha = (2N_0 - N)/2N_0 = 1 - N/2N_0$

that is to say $1 - \alpha = N/2N_0$

If it is assumed that $f = 2$ then

$DP_n = N_0/N$

5

This leads to:

$I_{COOH}/I_{CH2} = [(\varepsilon_1 - \varepsilon_2)/DP_n \; 2\varepsilon_0 + \varepsilon_0 \; / \; 2\varepsilon_0] \; x + \varepsilon_2 \; / \; DP_n 2\varepsilon_0$

(curve A)

$I_{OH}/I_{CH2} = \varepsilon_4 x/2\varepsilon_0 = \varepsilon'_2 DPn/2\varepsilon_0$ (curve B)

10

    Curves A and B are depicted in Figure 10. Where there exists an acid extremity and an alcohol extremity each having identical reactivities, the curves of the intensity ratios of the troughs should be straight

15 lines drawn as a function of the proportion of citric acid in the total acids.

Should one of the pendent alcohol or acid groups react, the functionality would no longer be 2 but would be a function of x, in which case the curves would no longer

20 be straight lines.

Where the two extremities are acids, the slope of the ratio I_{COOH}/I_{CH2} changes, whilst the straight line corresponding to $I_{OH}/I_{CH2} = \varepsilon_4 x/2\varepsilon_0$ passes through the origin.
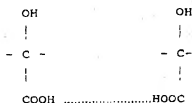
25 It can be noted that these curves are two straight lines, the curve B passing through the origin to within any variations in DP_n and any uncertainties in calculation.

It may therefore be assumed that DP_n is always
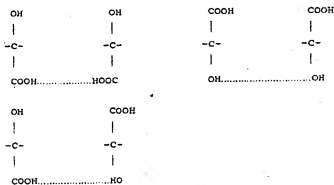
30 relatively identical to itself, and is therefore a

constant, except if the ratios $(\varepsilon_1 - \varepsilon_2)/\varepsilon_0$ and $\varepsilon_1/\varepsilon_0$ are very different. In this case very high variations in DP_n could result in very small variations in slope; this is the case if $(\varepsilon_1 - \varepsilon_2)/\varepsilon_0$ and $\varepsilon_1/\varepsilon_0$ are very small.

The hydrogen bonds are mainly of the following type:

$$
\begin{array}{ccc}
\text{OH} & & \text{OH} \\
| & & | \\
-\,\text{C}\,- & & -\,\text{C}- \\
| & & | \\
\text{COOH} & \cdots\cdots\cdots\cdots & \text{HOOC}
\end{array}
$$

This explains the high percentage of free OH groups with a small amount of citric acid, as well as the OH .... OH bonds.

With an increasing level of citric acid, three types of hydrogen bond coexist statistically. These bonds are as follows:

$$
\begin{array}{cccc}
\text{OH} & \text{OH} & \text{COOH} & \text{COOH} \\
| & | & | & | \\
-\text{C}- & -\text{C}- & -\text{C}- & -\text{C}- \\
| & | & | & | \\
\text{COOH} \cdots\cdots \text{HOOC} & & \text{OH} \cdots\cdots\cdots \text{OH}
\end{array}
$$

$$
\begin{array}{cc}
\text{OH} & \text{COOH} \\
| & | \\
-\text{C}- & -\text{C}- \\
| & | \\
\text{COOH} \cdots\cdots\cdots \text{HO}
\end{array}
$$

The presence of these three types of bond explains the displacement of the peaks as a function of the level of citric acid and "parasitic" bands such as those situated at 1800 cm^{-1} corresponding to a COOH .... HOOC bond explained below.

Having regard to the straight lines A and B obtained in Figure 10, it can be assumed that $\varepsilon_4 = \varepsilon_2 = \varepsilon_1 = \varepsilon_3$.

Which gives the following mathematical formulae:

$I_{COOH}/I_{CH2} = \varepsilon_3 \; x \; / \; 2\varepsilon_0 + \varepsilon_2 DP_n \; / \; 2\varepsilon_0$ and,

$I_{OHtotal}/I_{CH2} = \varepsilon_3 \; x \; / \; 2\varepsilon_0$

Giving $I_{OHlinked}/I_{CH2} = \varepsilon_3 (1-\alpha) \; x \; / \; 2 \; \varepsilon_0$, and

$I_{OHfree}/I_{CH2} = \varepsilon_3 \; \alpha \; x/2\varepsilon_0$

where α represents the percentage of free OH groups.

All this is validated by the fact that the point x = 0 on the curve IOH/ICH2 is situated on the curve I_{COOH}/I_{CH2} and by the fact that these two curves are linear. Thus it can be noted that the number of COOH and OH groups remains identical in ratio, except for the extremities, and that the pendent COOH and OH groups do not react during the esterification reaction.

II – Study of the infrared spectra in the 1700-1800 cm^{-1} region

Here the half bandwidths are used.

It was noted that citric acid (Figure 2) gives one band at 1730 cm^{-1} and another band at 1640 cm^{-1}, and that succinic acid gives two relatively close bands at 1705-1715 cm^{-1}.

A representation is assumed where the band is divided into a left-hand part and a right-hand part, the left-hand part corresponding to citric acid and esters, and the right-hand part to the superimposition of the esters, tertiary citric acid, primary citric acid and primary succinic acid.

If r represents the ratio of the right-hand half-width to the left-hand half-width, r can be defined by the following formula:

$r = [\text{dl ester } \varepsilon_1 + \text{dl ac.cit.tert. } \varepsilon_2 + \text{dl ac.ext. } \varepsilon] / [\text{dl ester } \varepsilon_1 + \text{dl ac.cit. tert. } \varepsilon_2]$

where:

- "dlester" is the half bandwidth of the ester,
- "dl ac.cit.tert." is the half bandwidth of the tertiary citric acid,
- "dl ac.ext." is the half bandwidth of the acids at the chain extremities.

The chain extremity is defined by N groups distributed as $Nx + N(1-x)$, where Nx corresponds to citric acid, and $N(1-x)$ to succinic acid.

The esters are defined by $2N_0-N$, if it is assumed that the esters have equal values.

The pendent citric acid is defined by N_0x.

It can therefore be written that:

$r-1 = 2 (\varepsilon_3 Nx + \varepsilon_4 N(1-x)) / (\varepsilon_1 (2N_0-N) + \varepsilon_2 N_0 x)$

that is to say $r-1 = 2 (\varepsilon_4 N + (\varepsilon_3-\varepsilon_4)Nx) / (\varepsilon_1 (2N_0-N) + \varepsilon_2 N_0 x)$

The degree of conversion α is defined by the ratio of esters created/acids initially present.

That is to say $\alpha = (2N_0-N) / 2N_0$

and the degree of polymerisation can be written:

$DP_n = 1/f (1 / (1-\alpha)) = 2 N_0 / 2N = N_0 / N$

The equation r-1 then becomes as follows:

$$r-1 = 2(\varepsilon_3 - \varepsilon_4)N \ /\varepsilon_2 No \ [(\varepsilon_4/(\varepsilon_3-\varepsilon_4))+x]/((\varepsilon_1/\varepsilon_2)(2-N/N_0) \ + \ x)$$

that is to say again

5 $$r-1 = (2(\varepsilon_3-\varepsilon_4) \ /\varepsilon_2 \ DP_n) \ / \ [(\varepsilon_4/(\varepsilon_3-\varepsilon_4))+x]/(\varepsilon_1/\varepsilon_2)(2-1/DP_n)+x]$$

The curve r-1 defined as a function of the ratio of moles of citric acid/moles of total acid is shown in
10 Figure 11.

Consequently the relationship is indeed of the type $(a+x)/(b+x)$. It is depicted in Figure 11.

15 In conclusion, the infrared study demonstrates the following points:

a) the polycondensation takes place in a linear manner whatever the amount of citric acid at the start,
20

b) the level of citric acid is high in proportion to the strength of the hydrogen bonds (the COOH and OH groups are very quickly bonded),

25 c) the polymerisation degree values DP_n seem close, and yet the calculations can result in very high variations in values of DP_n for small variations in ratio I, and this as a function of the values of ε,

d)   the solubility of the products passes through an optimum at around 28%.

DIFFERENTIAL ENTHALPIC ANALYSIS

This analysis shows the progressive disappearance of the melting peak with the progressive increase in the concentration of citric acid between each example 1 to 5.

The thermal behaviour of the copolymers in each example can be compared to that of the copolymers of the ethylene-vinylalcohol type where the melting peak disappears when the concentration of vinylalcohol increases, the polyvinylalcohol not melting.

The thermal behaviour of these polymers also recalls that of the copolymer blocks.